Supporting Information

Crystalline Quantum Dot of Covalent Organic Framework for Fast and Sensitive Detection of Uranium

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Experimental Section

Reagents

The 2,4,6-triformylphenol, tris(4-aminophenyl)amine, all metal oxides and nitrates used in this research were purchased from Aladdin Chemistry Co., Ltd. (China). N,N-Dimethylformamide, dichloromethane, ethanol, acetone, acetic acid, sodium hydroxide and nitric acid were bought from Chengdu Kelong Chemical Reagent Factory. All reagents were of AR grade or of the better purity available and used as received without further purification.

Characterization methods

Powder X-ray diffraction (PXRD): PXRD pattern was collected on Malvern Panalytical Empyrean diffractometer (Netherlands) using Cu Kα radiation (40 kV, 40 mA) at room temperature.

N₂ adsorption-desorption: The N₂ adsorption-desorption isotherms were measured by Micromeritics ASAP 2020 (USA) at 77 K and the sample was activated and outgassed at 150 °C for 2 h before measurement. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. The Brunauer Emmett-Teller (BET) surface area and total pore volume were calculated from the N₂ sorption isotherms at 77 K.

Transmission Electron Microscopy (TEM): HR-TEM images were recorded using FEI Tecnai G2 TEM (USA) at an accelerating voltage of 300 kV.

Dynamic Light Scattering (DLS): the DLS measurement was carried out using a zetasizer nanosystem (Malvern Instruments Ltd).

Atomic Force Microscopy(AFM): AFM (Bruker Innova, Switzerland) scans were collected under tapping mode in air.

Fourier transform infrared (FT-IR): The IR (KBr pellet) spectra were recorded (400-4000 cm⁻¹ region) on Nicolet Nexus 670 spectrometer (USA).

Solid-state NMR: Solid ¹³C NMR experiments were carried out on a Bruker Avance III 500MHz.

Thermogravimetric analysis (TGA): TGA were carried out on a Shimadzu DTG-60(H) analyzer (Japan) under N₂ atmosphere at a heating rate of 10° C min⁻¹ within a temperature range of 30-800°C.

Elemental analysis (EA): Elemental analysis was performed on a CARLO ERBA 1106 (Italy) for C, H, and N.

UV spectra: Shimadzu UV-3600 spectrophotometer (Japan) was used to measure the transmittance of the reaction band during the generation of QDCOF.

Fluorescence spectra: Fluorescence spectra were recorded at room temperature using a SHIMADZU RF-5301PC fluorescence spectrophotometer (Japan).

Inductively coupled plasma atomic emission spectroscopy(ICP-AES): the concentrations of all the metal ions used in this work were analyzed by ICP-AES (Optima 8000, PerkinElmer, USA) using the standard curve method.

X-ray photoelectron spectroscopy (XPS): XPS spectra was recorded on a Kratos ASAM800 spectrometer (UK).

Synthesis of QDCOF

17.8 mg (0.1 mmol) 2,4,6-triformylphenol was dissolved in a mixture of 2 mL DMF and 80 mL DCM in a beaker. And then 40 mL 12M acetic acid were slowly added in the beaker. 29 mg (0.1 mmol) tris(4-aminophenyl)amine was dissolved in 50 mL DMF and slowly added dropwise to the surface of acetic acid. The above solution was standing at room temperature for 3 days. After the reaction, the brown powder was obtained by vacuum distillation and washed with EtOH, acetone and deionized water sequentially until the filtrate was neutral and colorless. The resulting powder was further purified by Soxhlet extraction with methanol for 72 h and then freeze-dried at - 50 °C for 24 h. The resulting material was named QDCOF and the yield was about 29%.

In the experiment, the monomer Sa was dissolved in a mixture of DCM and DMF in a vessel, and then some high-concentration acetic acid was added slowly from the top. Finally, a solution of TAPA in DMF was added dropwise to the above solution. As TAPA

moved to the middle layer and reacted with acetic acid to form acetate, the color of the upper layer gradually changed from light red to green. At the same time, the monomer Sa in the lower layer also diffused slowly to the intermediate layer, met and reacted with TAPA, thereby generating a large number of small QDCOF particles in the buffering reaction band.

Quantum yield (QY) calculation

Quinine sulfate in 0.10 M H₂SO₄ solution was used as a standard. The QY of QDCOF (in water) were computed according to the following formula:

$$\Phi = \Phi_R \times \frac{l}{l_R} \times \frac{A_R}{A} \times \frac{\eta^2}{{\eta_R}^2}$$
(1)

where Φ is the quantum yield, *I* is the measured integrated emission intensity, η is the refractive index of the solvent, and *A* is the optical density. The subscript *R* refers to the standard index of quinine sulfate (calculation data are listed in Table S2).

Fluorescence response experiment

Dispersion of QDCOF was prepared in H₂O and stock solutions of UO₂(NO₃)₂ (~0.2 mmol/L) was prepared in H₂O of different pH. The fluorescence spectra were recorded immediately after an appropriate aliquot of the stock solution of uranyl ions was added. Each test was repeated at least for three times to get concordant values. All the measurements, unless otherwise noted, were excited at λ ex = 410 nm and the corresponding emission wavelength was tested from λ em = 440-580 nm. The corresponding limit of detection (LOD) was determined using the equation LOD = 3 × S.D./k, where k represents the slope of the curve equation, and S.D. is the standard deviation for F₀ (the fluorescence intensity of QDCOF in the absence of UO₂²⁺). Calculation data are listed in Table S3.



Fig. S1 HRTEM image of QDCOF.



Fig. S2 The particle size distribution of QDCOF from DLS. The average particle size is about 3.8 nm consistent with the size from TEM.



Fig. S3 FT-IR spectra of TAPA, Sa and QDCOF. The peaks of $-NH_2$ (~3400 cm⁻¹) and -CHO (~1689 cm⁻¹) disappeared, and a new peak appeared at 1611 cm⁻¹ attributed to the newly generated C=N band after the condensation reaction.



Fig. S4 Solid-state ¹³C NMR of QDCOF.



Fig. S5 TGA curves of TAPA, Sa and QDCOF. In contrast to the monomers, the thermal stability of QDCOF is significantly improved and the sample maintains more than 80% of its weight up to 500°C.



Fig. S6 Fluorescence curves with different concentration of QDCOF.



Fig. S7 Relative fluorescence intensity of QDCOF at different time irradiated by the Xe lamp (F_0 is the fluorescence intensity of QDCOF at 0 min). After continuously irradiated by the Xe lamp of the fluorescence spectroscopy for nearly 1 h, the fluorescence intensity of QDCOF aqueous solution did not decrease distinctly, indicating its strong anti-photobleaching ability.



Fig. S8 Photo images of QDCOF in neutral H₂O over various times. Aqueous solution of QDCOF exhibits excellent dispersibility and stability, which can be observed with no precipitation over 3 months.



Fig. S9 FT-IR spectra of QDCOF before and after soaking in H₂O for 3 months and 1M HNO₃ for 1 day. The spectra of QDCOF after soaking had no obvious difference with that of the original material, which showed that QDCOF has good stability in water and acid solution. The stability of QDCOF may be caused by the existence of hydrogen bond and the enol-keto tautomerization.



Fig. S10 The species distribution of uranium ($c_0 = 45 \ \mu mol \ L^{-1}$, T = 298K) under different pH conditions. Uranyl ions are normally stable in acidic environment and tend to precipitate in alkaline solutions. Therefore, the acidity of sensing solution of uranyl ion was in acidified solution.



Fig. S11 Fluorescence response of QDCOF aqueous solution upon the gradual addition of UO_2^{2+} at pH 7.



Fig. S12 Fluorescence response of QDCOF aqueous solution upon the gradual addition of $UO_2^{2^+}$ at pH 5.5.



Fig. S13 Fitted curve of fluorescence of QDCOF aqueous solution upon the gradual addition titration of UO_2^{2+} at pH 4.5 (F₀ is the fluorescence intensity of QDCOF in the absence of UO_2^{2+}).



Fig. S14 Fitted curve of fluorescence of QDCOF aqueous solution upon the gradual addition titration of UO_2^{2+} at pH 5.5 (F₀ is the fluorescence intensity of QDCOF in the absence of UO_2^{2+}).



Fig. S15 Fitted curve of fluorescence of QDCOF aqueous solution upon the gradual addition titration of UO_2^{2+} at pH 7 (F₀ is the fluorescence intensity of QDCOF in the absence of UO_2^{2+}).



Fig. S16 Fluorescence response of QDCOF in the presence of different metal ions, including the common high released nuclear reaction fission products Cs^+ and Sr^{2+} , the element Co^{2+} that can be used as standard radiation source for γ ray, and the actinide radioactive element Th^{4+} . F₀ is the fluorescence intensity of QDCOF in the absence of metal ions and the concentration of each metal ion is about 18 μ M.



Fig. S17 XPS spectra of QDCOF before and after quenching. Compared to the original QDCOF, two obvious new U 4f peaks in the pattern of QDCOF after quenching revealed the existence of uranium in the sample after quenching.



Fig. S18 High-resolution XPS spectra of U 4f for QDCOF after quenching.



Fig. S19 High-resolution XPS spectra of O 1s for QDCOF before and after being quenched by U. The peaks at 398.80 and 399.48 eV are ascribed to C=N and C-N, corresponding to the enol- and keto-forms in the tautomerization, respectively.



Fig. S20 High-resolution XPS spectra of O 1s for QDCOF before and after being quenched by U. The peaks at 532.53 and 530.98 eV are asigned to C-OH and C=O, corresponding to the enol- and keto-forms in the tautomerization, respectively.

Element	Experimental value (%)	Theoretical value (%)
С	73.7	74.1
Ν	11.3	12.8
0	9.8	8.4
Н	5.2	4.7

 Table S1 Experimental and theoretical values of EA for QDCOF.

Table S2 Quantum yields parameters of QDCOF using quinine sulfate as reference.

Sample	Integrated emission	Abs. at 320 nm	Refractive index	Quantum
	intensity (I)	(A)	of solvent (η)	yields (Φ)
QDCOF	19663	0.116	1.33	0.01
Quinine sulfate	508650	0.053	1.33	0.55

Table S3 Calculation parameters of LOD in QDCOF aqueous solution upon thegradual addition titration of $UO_2^{2^+}$.

F ₀			S.D.*	k*	LOD (µM)	LOD (ppb)		
9226	9228	9235	9210	9211	11.0227	-273.12	0.12	28.6

* S.D. is the standard deviation for F_0 and k represents the slope of the curve equation in Fig. S13.